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ULTRAVIOLET ABSORPTION SPECTRUM OF ACETOPHENONE

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Plate VII

ABSTRACT The absorption spectrum of acetophenone was studied at different temperatures and with different lengths of the absorbing column. There are four regions of absorption, two in the region of 2400Å, third at about 2800Å and the fourth at about 3200Å New bands in absorption have been observed in these studies and an interpretation for the same is discussed.

INTRODUCTION

Acetophenone forms an important starting point for a class of compounds in which C = O is conjugated to phenyl ring. Benzaldehyde, which is the first member of such a class, has been extensively investigated by various workers The absorption spectrum of acetophenone was studied by Kato and Someno (1938) in liquid solution and absorption bands were reported by them at wave numbers 34900, 35900 and 37000 It was further studied by Deb (1951) and he has reported three broad bands with centres at 35744, 38748 and 40277 cm $^{-1}$ respectively. The ultraviolet absorption and fluorescence was studied by Vanselow and Duncan (1953). They have observed at room temperature (about 1 mm pressure) three bands at 2832, 2770 and 2695Å in a 20 cm path of the absorbing column. They also report that a new band appears at about 60 mm pressure with centre at about 3250 Å. Apart from earlier work, absorption of acetophenone in the vapour state has been recently investigated by Imanishi, Semba, Ito and Anno (1952). These workers, as also the work on solution spectrum, have clearly established that the complete ultra-violet spectrum consists of three regions of absorption. The longest wave length region near 3200 Å is assigned to an $n-\pi$ transition of the C = O group. The region between about 2900-2400Å corresponds to the 2600Å absorption of benzene suitably modified by substitution. Absorption on the lower ultraviolet below 2400Å has been assumed to correspond to the 1900 Å benzene band and is tentatively assigned due to $N-V$ transition of carbonyl group. Imanishi *et al.* have studied the absorption system between 2900–2400Å. Duncan *et al.* were mainly concerned with the 3200Å absorption system and the corresponding fluorescence of this molecule. The 2800Å band

system has been studied in the present investigations at various temperatures and at different path-lengths.

EXPERIMENTAL

Experiements have been carried out at room temperature (30°C) using saturated vapour of acetophenone in columns of lengths varying from 2 cm to 4 m. Experiments were carried out also with a tube in which the vapour pressure was that saturated at 60°C and the tube was heated to various temperatures. A hydrogen lamp was used to give the continuum. A Hilger medium quartz spectrograph and B 20 plates were used. The wide diffuse bands were photographed on a Hilger small quartz spectrograph. At least three plates were measured on a comparator reading to 0.001 mm. As the bands are diffuse readings were taken at the centre of the bands The liquid used was distilled at the temperature corresponding to the boiling point and the first and the last portions of the distillate were discarded collecting the liquid only after the first portions were removed. The liquid was put in the bulb and quartz windows were attached at both ends by sealing wax and the open end of the bulb was connected to a vacuum pump and then sealed off. A comparison spectrum of copper was superposed in the centre.

EXPERIMENTAL RESULTS

With 2 cm cell and temperature of the liquid at 24°C at an exposure time of 20 minutes, an absorption band was observed with its centre at 2389 Å (Plate VII, Fig. 1). With 5 cm length of the absorbing column at room temperature only two bands at 2826 Å and 2752 Å were observed. When the length of the column was 50 cm, all bands mentioned in the 2800 Å region appeared at room temperature. When the temperature of the bulb was maintained at 5°C bands at 2826 and 2752 Å were still there and accompanied by another diffuse band with centre at 2389 Å and a very broad diffuse band from 2330Å to 2249 Å (Plate VII, Fig. 2) By increasing the length of the absorbing column to 100 cm or more, the bands as mentioned in the table below appeared. (Plate VII, Fig. 4 & 5. When the length of the absorbing column was 4 metres the diffuse band with centre at 3250 Å was clearly seen (Plate VII, Fig. 3). On heating the cell so that the temperature of the bulb and the cell was the same no additional bands were observed on the longer wave length side of the (0—0) band though the temperature was raised from 36°C to 110°C (Plate VII, Fig. 6). The data on the bands are given in Table 1.

DISCUSSION

The spectrum can be divided into two types of bands.—A prominent set of diffuse bands which are very similar in nature and of which the first member is the 0- 0 band; and three sets of a group of three comparatively sharp bands in between

TABLE I

Wave length (Å) in air	Nature of band	Wave number in vacuo	Assignment
2826	b.d.	35375	0,0
2797	s.d.	35742	0,+367
2790	s.d	35831	0,+456
2781	s.d	35947	0, +572
2752	b.d.	36326	0,+951
2725	s d	36686	0, +951 +360
2718	s.d.	36780	0,+951+454
2709	s.d.	36903	0,+951+577
2681	b.d.	37288	0, +951 +962
2656	s.d.	37639	0,+2(956)+351
2649	s.d.	37738	0,+2(956)+450
2641	s.d.	27853	0, +2(956)+565
2614	b d.	38244	0, +2(956) +956

* b.d. = broad diffuse. s.d. = sharp diffuse.

the diffuse bands. The disposition and nature of these bands seem to indicate that they do not belong to the series of diffuse bands and although belonging to the same electronic transition they form a different series.

Acetophenone belongs to the C_s symmetry group and as such has only two symmetry types, namely, A' and A'', symmetric and anti-symmetric to the plane of symmetry. The transitions between these are allowed. The successive reduction of symmetry from D_{6h} of benzene to acetophenone C_s through C_{2v} shows that the $A_{1g}-B_{2u}$ transition of benzene becomes $A'-A'$ under the reduced symmetry and is hence allowed by selection rules. The assignment of (0—0) band is in agreement with Imanishi *et al.* whose selection of the band was, however, quite arbitrary. Absorption was recorded at various temperatures and no extension of the 2800 system was found beyond the band at 2826Å The intensity distribution in the system of bands at higher temperatures when compared to that obtained at lower temperatures showed that the first strong band at 35375 cm^{-1} is the 0—0 band of the system.

Fig. 1

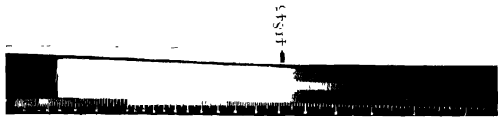

Fig. 2

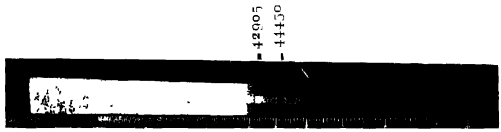

Fig. 3

Absorption spectra of acetophenone

Fig. 1. 2389 A U. band (41845 cm^{-1})

,, 2. Broad diffuse band

,, 3. Diffuse band at 3250 A U. (30760 cm^{-1})

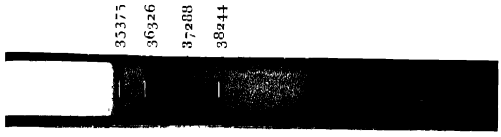

Fig. 4

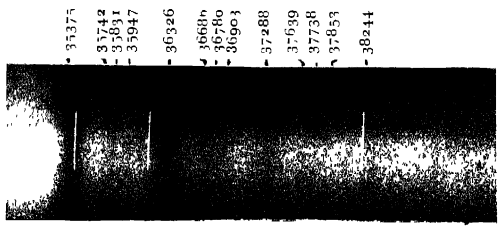

Fig 5.

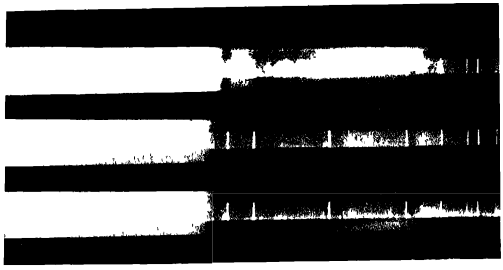

Fig. 6

Fig 7

Fig 8

Absorption spectrum of acetophenone

Fig. 4 Contact print 2800 system of bands.

,, 5. Enlarged print showing sharp diffuse bands

,, 6. Absorption at 36°C

,, 7. Absorption at 80°C

,, 8 Absorption at 110°C

It is significant to note that even at a temperature of 110°C no further bands are observed on the longer wave length side of the 2826 Å band. This is in contrast to benzaldehyde where quite a large number of small frequencies in the ground state are excited with increase of temperature or path length.

The principal progression with frequency of 956 is observed as in most cases of substituted benzene. This progression has been explained as due to the excited state frequency corresponding to the totally symmetric frequency of about 1000 cm^{-1} in the ground state which corresponds to the totally symmetric vibration frequency 992 cm^{-1} in benzene. Long progressions of bands corresponding to excitation of this type of vibration have been observed in most of the simple substituted benzenes.

The ground state frequencies corresponding to the excited ones of the order of 360, 450 and 570 giving rise to the three comparatively sharp bands are not excited at the temperatures employed in the present experiments. This is rather peculiar to the molecule because similar ground state vibrations have been observed in the spectrum of benzaldehyde (Garg, 1953).

Of these three vibrations two must correspond to the two vibrations arising out of the 606 cm^{-1} e_{2g} degenerate benzene vibration. Imanishi *et al.* have assigned 360 and 570 to the excited state frequencies corresponding to 371 and 617 in the ground state, these being the two vibrations corresponding to 606 of benzene. Under the C_s symmetry both belong to a' symmetry and thus give rise to bands of about the same intensity That the assignment is essentially correct can be seen by comparison with the spectrum of benzaldehyde and other benzene derivatives The smaller of the two frequencies shows a decrease with the increasing weight of substituent and the value calculated according to formula given by Garg comes to be of the order assumed here. The higher frequency component of the split frequency is rather invariable with the substituent Both show appreciable depolarization in Raman effect and hence belong to a' symmetry.

The third frequency (450) may be excited frequency of 588 in the ground state, in analogy with the spectrum of acetaldehyde where Rao and Rao (1954) have assigned 527 cm^{-1} and the corresponding ground state frequency 562 cm^{-1} to C—C = O bending vibration of a' type. This is a very prominent frequency in the acetaldehyde spectrum.

The excited frequency ~570 in acetophenone corresponds to the excited frequency ~544 in benzaldehyde in which it occurs only in combination with the (0– 0) band. In acetophenone, however, the vibration (~570) is present associated with successive quanta of the totally symmetric vibration. This frequency therefore corresponds to the e_{2g} of benzene where under the D_{6h} symmetry it is excited

only to one quantum for the $A_{1g}-B_{2u}$ transition. It appears that whereas benzaldehyde still retains some part of residual benzene character, acetophenone seems to have lost all of it.

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